

PCT

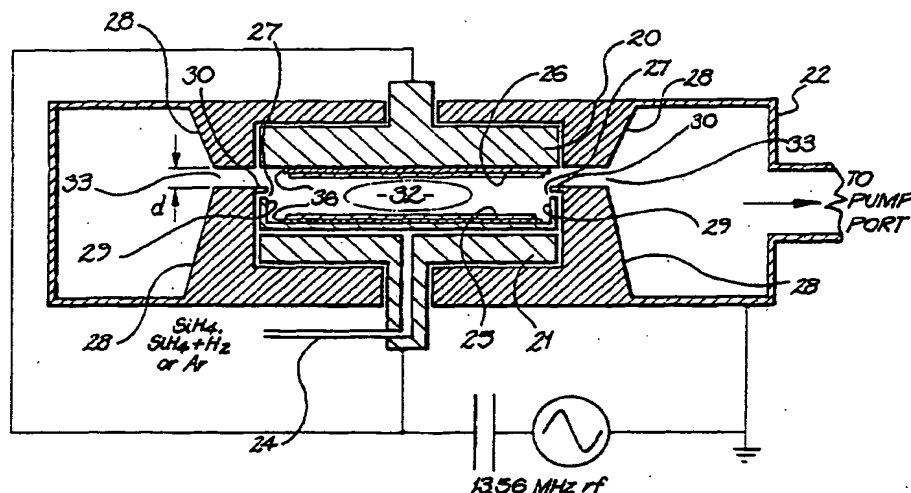
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C23C 16/24, 16/52, H01L 21/203		A1	(11) International Publication Number: WO 99/28528
			(43) International Publication Date: 10 June 1999 (10.06.99)
(21) International Application Number: PCT/AU98/00974		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 24 November 1998 (24.11.98)			
(30) Priority Data: PP 0554 26 November 1997 (26.11.97) AU			
(71) Applicant (for all designated States except US): PACIFIC SOLAR PTY. LTD. [AU/AU]; 82-86 Bay Street, Botany, NSW 2019 (AU).			
(72) Inventors; and (75) Inventors/Applicants (for US only): GREEN, Martin, Andrew [AU/AU]; 10 Blandford Avenue, Waverley, NSW 2024 (AU). BAZYLENKO, Michael [AU/AU]; 15A Deakin Street, Forestville, NSW 2087 (AU). ZHANG, Fengming [AU/AU]; 1/58 Grosvenor Crescent, Summer Hill, NSW 2130 (AU). SHI, Zhengrong [AU/AU]; 37 Princes Mary Street, Beacon Hill, NSW 2100 (AU).		Published With international search report.	
(74) Agent: F.B. RICE & CO.; 605 Darling Street, Balmain, NSW 2041 (AU).			

(54) Title: HIGH RATE DEPOSITION OF AMORPHOUS SILICON FILMS



(57) Abstract

Hydrogenated amorphous silicon films are deposited simultaneously on two metal or dielectric substrates (25, 26, 43, 44) from a radio frequency glow discharge (32) maintained in a mixture of gases or vapours with at least one of them containing silicon in its molecule. The discharge (32) is maintained between two mutually symmetric, radio frequency powered electrodes (20, 21, 41, 42) enclosed in a grounded chamber (22, 40) and isolated from it, with one substrate placed on the internal side of each of the electrodes (20, 21, 41, 42). All surfaces of the electrodes (20, 21, 41, 42) except the two surfaces where the substrates (25, 26, 43, 44) are placed, are enclosed in grounded metal parts (28), some of which may be chamber walls, with a gap between them sufficiently small to prevent discharge formation at the process pressures. The method can be extended so that 2n (n = 1, 2, 3...) substrates are deposited simultaneously in each of n pairs of the electrodes such as by using a "box-coater" arrangement particularly well suited to the hollow cathode configuration.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MV	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

High rate deposition of amorphous silicon films

Introduction

The present invention relates generally to the field of Plasma Enhanced Chemical Vapour Deposition (PECVD) and in particular, the invention provides a method of depositing high quality hydrogenated
5 amorphous silicon films.

Hydrogenated amorphous silicon (a-Si:H) has been used extensively in many large-area device applications, such as solar cells, photoreceptors, flat-panel displays, page-wide document scanners and printer heads. Its low deposition temperature makes it ideally suited for
10 large area microelectronic devices, where low-cost glass is often utilised as a substrate. Much of the success of a-Si:H originates from its low defect density, which makes it behave like a true semiconductor that exhibits doping effects. There is additional interest in the use of such amorphous silicon films as precursors for higher performance polycrystalline silicon
15 films for similar applications. For industrial applications, high rate deposition of good quality a-Si:H film material is desirable.

Background to the Invention

At a simple phenomenological level, the deposition rate of amorphous silicon from SiH_4 discharge (pure or diluted) is determined by
20 the rate of SiH_4 supply to the discharge chamber (SiH_4 flow rate) and the rate of silane decomposition in the plasma. The latter is related to the amount of deposition precursors (SiH_x) generated in plasma volume per second. In conventional PECVD systems the silane decomposition rate (and therefore the deposition rate) can be increased by increasing the rf
25 (radio frequency) power coupled into the discharge. Such increase, however, is usually limited by an onset of gas phase polymerisation or powder formation which occurs above a certain rf power threshold resulting in a large number of clusters being incorporated in the film, as well as a yellow powdery deposit on all the chamber surfaces. This has
30 been the main reason for the use of a relatively low a-Si deposition rates ($< 10 \text{ \AA/s}$) in conventional PECVD systems. An alternative way of increasing the deposition rate is by increasing the silane flow rate. This may help to increase the deposition rate significantly, but is only practical to a point where increase in productivity is negated by an increase in the
35 cost of the silane consumption. In this process the silane utilisation factor

(percentage of silicon in the total silane flow deposited on the substrates), which is already small in a conventional process (<5%), drops further, implying an increase in the process-associated material costs.

Additionally, the deposition uniformity can also become a problem as the residence time of the deposition precursors becomes small at very high flow rates. An increase in the rf power (increasing the silane decomposition rate) can improve the utilisation factor, but gains are again limited by the powder onset threshold. The suppression of the powder formation thus appears to be the key to developing both high rate and high efficiency (in terms of silane consumption) deposition processes.

A number of methods have been reported, which allow one to shift the powder onset threshold towards higher rf powers thus achieving high silane decomposition rates in a powder-free regime. They include the use of a higher frequency (up to 110 MHz as opposed to 13.56 MHz) [M. Heintze et al, Mat. Res. Soc. Symp. Proc. 297, 50 (1993)], high density (e.g. Electron Cyclotron Resonance) plasma sources [S. Guha et al, Appl. Phys. Lett. 66, 595 (1995)] to reduce the process pressure (thus reducing the probability of gas phase nucleation), increasing the reactor temperature [R. Banerjee et al, J. Appl. Phys. 74, 4540 (1993)] and modulation of the rf signal (which drives the discharge) on a scale of a few milliseconds [J. P. M. Schmitt et al, Mat. Res. Soc. Symp. Proc. 219, 631]. The effectiveness of each of these methods is related to the mechanisms of powder formation. Some of these methods have scaling-up problems, such as deposition uniformity over a large area and complication of the reactor design.

Summary of the Invention

According to a first aspect, the present invention provides a method of deposition of hydrogenated amorphous silicon film onto a substrate from a radio frequency glow discharge, the method including, placing the substrate on or near an internally facing surface of a first electrode of a pair of mutually symmetric, radio frequency powered, electrodes enclosed in and isolated from, a grounded chamber, evacuating the chamber, and introducing into the chamber, a gas or vapour or a mixture of gasses and/or vapours including a source of silicon atoms and operating the chamber with a power to pressure ratio determined to allow

rapid (ie. $>15 \text{ \AA/sec}$) formation of amorphous silicon on the substrate with dominant monohydride (Si:H) bonds and low particle formation.

According to a second aspect, the invention provides a Plasma Enhanced Chemical Vapour Deposition (PECVD) system for depositing
5 hydrogenated amorphous silicon films including a chamber enclosing a pair of mutually symmetric, opposed electrodes, at least one of the opposed electrodes being arranged to receive a deposition substrate on or adjacent to its surface, the chamber including an output port connected to a vacuum pump and an input port connected to a supply of a gas or vapour
10 or gases and/or vapours including a source of silicon atoms, and a radio frequency power supply connected between the chamber and the pair of symmetric electrodes and control means for setting a pressure to power ratio at a value determined to allow rapid formation of amorphous silicon on the substrate with dominant monohydride (Si:H) bonds and low
15 particle formation.

Throughout this specification and claims "low particle formation" means particle formation below 5×10^4 particles/cm².

In embodiments of the invention surprisingly high deposition rates of $0.5 \mu\text{m/min}$ have been achieved while maintaining good material quality.
20 The presence of a dominance of monohydride (Si:H) bonds is determined by Fourier Transform Infra Red (FTIR) absorption, where a dominant peak is observed at 2000 cm^{-1} rather than 2100 cm^{-1} .

Preferably, the chamber is grounded and the opposed electrodes are maintained at the radio frequency potential of the power supply.
25 Preferably also each of the opposed electrodes is arranged to receive a substrate on its respective internally facing surface such that two substrates may be coated simultaneously. In the preferred embodiment, all surfaces of the opposed electrodes, except those covered by a substrate to be deposited onto are enclosed in grounded metal shields separated
30 from the respective surfaces by a gap sufficiently small to prevent discharge formation at the process pressure.

In the preferred embodiment, a plurality (n) of pairs of opposed electrode surfaces are provided in the chamber with each pair of opposed surfaces arranged to receive a respective pair of substrates for deposition.
35 In one embodiment, each pair of opposed electrode surfaces is provided by a separate pair of electrodes located in a grounded enclosure within the

chamber and electrode pairs are removable individually as a module for substrate attachment and removal. Preferably, this is achieved by providing two electrodes fixed to and insulated from a grounded metal frame to form a portable process vessel which is arranged to be loaded into the chamber for deposition and then unloaded from it. In another embodiment, both sides of each electrode (except for end electrodes) are arranged to accept a substrate for deposition with each surface of each electrode providing one of a different pair of opposed surfaces to the other surface of the same electrode, and each electrode is removable for attachment and removal of substrates.

In one embodiment, substrate temperature is controlled by grounded heaters associated with each electrode. In the case of single sided electrodes, heaters may be located behind each electrode, shaped to conform with the shape of the back surface of the electrode, and in the case of double sided electrodes, the electrodes may have internal spaces in which the heaters are located. In other embodiments the temperature can be controlled by introducing hot gas into the chamber.

In the preferred embodiment, discharge confining elements, preferably of metal are located within the chamber and connected to the electrodes and/or the chamber to control the discharge characteristics, deposition process and film characteristics.

The confining elements are preferably configured to preserve the symmetry of the system with respect to the substrates. In the case where the confining elements are connected to the electrodes, they are shielded from the grounded chamber by shielding elements conforming with back surfaces of the confining elements and separated from the confining elements by a gap sufficiently small to prevent discharge formation in the gap.

Film characteristics may also be controlled by controlling the ion bombardment energy on the surface of the substrate. In embodiments of the invention, this is achieved by introducing an equal gap between each of the substrates on each pair of opposed electrode surfaces and the respective electrode surface, and varying the gap to achieve the desired characteristics. In one embodiment, the gaps between the substrates and the respective electrodes are filled with dielectric material.

Embodiments of the invention may use silicon tetrahydride (silane) as the silicon source and the source gas may be diluted with a noble gas or hydrogen or both.

In the preferred embodiment, the ratio W^k/P , where W is power density on the substrate (W/cm^2), P is the gas pressure (pa) and k is a co-efficient ranging from 0.5 to 4.0, is kept below a predetermined, empirically established, value in order to prevent the degradation of film quality due to an onset of gas phase polymerisation. The co-efficient k determines the shape of the boundary between "power" and "no powder" regions in the power density/pressure function as illustrated in Figure 11. Preferably, in the chamber described herein, the preferred range of the value k is 1.47 to 1.56, but may vary for other chambers and must be determined empirically. The value for W^k/P is lower, for increased discharge confinement and higher for increased total gas flow rate and/or increased silane dilution with a noble gas or hydrogen or both and in the experimental HCPECVD system is in the range from 0.25 to 2.04 as shown in Figure 11.

Brief Description of the Drawings

Embodiments of the invention will now be described, by way of example, with reference to the accompanying drawings in which:-

Figure 1 schematically illustrates a conventional prior art Plasma Enhanced Chemical Vapour Deposition (PECVD) System;

Figure 2 schematically illustrates a Hollow Cathode PECVD System according to an embodiment of the present invention;

Figure 3 diagrammatically illustrates a Hollow Cathode PECVD System according to an embodiment of the invention showing optimising features;

Figure 4 graphically illustrates A-Si deposition rate and utilisation factor as a function of silane flow rate for a confinement gap of 5mm, an Ar flow rate of 60sccm, an operating pressure of 1Pa and an rf input power of 500w;

Figure 5 graphically illustrates A-Si deposition rate and utilisation factor as a function of silane flow rate for a confining gap of 2.5mm with an Ar flow rate of 60sccm an operating pressure of 1Pa and an rf input power of 500w;

Figure 6 graphically illustrates A-Si deposition rate and utilisation factor as a function of discharge confining gap (d) with a silane flow rate of 40sccm, and Ar flow rate of 60sccm, operating pressure of 1Pa and an rf input power of 500w;

5 Figure 7 graphically illustrates A-Si deposition rate and utilisation factor as a function of rf power with a silane flow rate of 40sccm, an Ar flow rate of 60sccm and an operating pressure of 1Pa;

Figure 8 is a simplified perspective view of a Hollow Cathode PECVD box coater according to an embodiment of the invention;

10 Figure 9 is a cutaway diagram of a module from the box coater of Figure 8;

Figure 10 diagrammatically illustrates the Hollow Cathode PECVD systems of Figure 3 with substrates separated from their respective electrodes to control ion bombardment energy at the substrate surface; and

15 Figure 11, (a), (b) and (c) illustrate 3 different sets of operating conditions for the hollow cathode PECVD system of the present invention, showing the values of W^k/P at which the onset of powder formation occurs.

Detailed Description of the Embodiments

20 An a-Si:H deposition process, employing a Hollow Cathode PECVD (HCPECVD) is disclosed, which has a configuration quite similar to conventional diode type of PECVD reactor and operates at conventional frequency of 13.5 MHz. This technique has inherent advantages in terms of achieving high a-Si:H deposition rates in a powder-free regime (compared with conventional PECVD) due to:

25 - lower operating pressures
 - higher plasma density and higher ion flux on the surface of the growing film (this can be partially achieved in conventional PECVD by increasing the rf frequency).

30 Additionally, a high level of discharge confinement inherent to the HCPECVD system can provide high values of the silane utilisation factor (>50%).

Hollow Cathode principle

35 The use of the hollow cathode principle for rf discharges was first suggested in 1983 [C M Horwitz, Appl. Phys. Lett. 43, 977.(1983)] (before this report, the term "hollow cathode" was associated exclusively with dc

discharges)(see also US Patent No 4521286). The main difference between conventional PECVD and HCPECVD is in the electrical connection of the two opposing electrodes (Fig. 1). Referring to Figure 1, in conventional PECVD, one of the two electrodes 20 is rf powered, while the other electrode 23 and the rest of the chamber 22 are grounded. Referring to figure 2, in HCPECVD, both electrodes 20, 21 are rf powered while the chamber is grounded. The increase in the plasma density achieved with the Hollow Cathode configuration is attributed to the so called "electron mirror" effect [C M Horwitz 1983], in which a negative self-developed bias voltage on the two opposing rf powered electrodes both helps to increase density of the high energy electrons (responsible for ionisation) and to reduce their recombination rate. The hollow cathode effect can be enhanced by appropriate discharge confinement which results in an increase in the plasma density, an increase in the ion flux on the electrodes and a decrease in the average ion energy (for the same input power)

The use of HCPECVD for a Si deposition was reported by C M Horwitz and Dr. D R McKenzie, [Applications of Surface Science 22/23, 925(1985)] and C M Horwitz, [J. Vac. Sci. Technol. 7, 443 (1989)]. In the first instance a deposition rate of $0.1 \mu\text{m}/\text{min}$ was achieved, but the hollow cathode discharge zone was not confined and conventional discharge above the top electrode was not suppressed thus limiting further increase in the deposition rate and reducing the silane utilisation factor. Also, the low photoconductivity of the deposited films suggested somewhat poor quality of the produced a-Si:H material. In the second instance deposition rates as high as $1 \mu\text{m}/\text{min}$ were reported, but these high rate results were obtained under conditions of intense gas phase polymerisation and powder formation. The a-Si materials produced in this way have no practical device applications due to the poor material quality. Moreover, the purpose of that work was to obtain information about the plasma density by monitoring the a Si deposition rate, rather than to develop a practically useful process.

Deposition of a-Si:H by an improved HC PECVD system

Embodiments of the present invention provide a practical approach to using the Hollow Cathode system for high rate and device quality a-Si:H deposition including new chamber designs and chambers

suitable for processing multiple large area substrates 25, 26. A process with a-Si:H deposition rate of 0.3-0.5 $\mu\text{m}/\text{min}$ in a powder-free regime and the utilisation factor as high as 60 % have been developed and demonstrated in a specially constructed HCPECVD system.

5 The optimised design of the Hollow Cathode deposition chamber used for this high rate a-Si:H deposition is shown in Figure 3. Silane, diluted with argon or hydrogen, is supplied via an inlet port 24 to the opposite side of the lower electrode 21, and enters the Hollow Cathode discharge zone from the circumference 27 of the lower electrode 21. This
10 gas delivery configuration provides both good deposition uniformity and high silane utilisation since the silane decomposition starts to occur in the immediate vicinity of the electrodes. Guard rings 28 and confining ring 29 help maintain the discharge in close proximity to the electrodes 20, 21 and respective substrates 26, 25 and the lateral extension 30 of the lower guard
15 ring 28 (which is grounded) above the confining ring 29 of the bottom electrode 21 serves two purposes: it redirects the gas flow to the discharge zone 32 and prevents formation of a subsidiary (shunting) discharge between the top electrode 20 and the confining ring 29 of the bottom electrode 21. The discharge confinement (and therefore plasma density)
20 can be varied by varying the gap 33 between the guard rings 28. The smaller the gap 33 the higher the confinement and the higher the plasma density. In the HCPECVD system of this embodiment a typical deposition rate is 0.3-0.45 $\mu\text{m}/\text{min}$ is obtained for a silane flow rate of 40 sccm (depending on the discharge confinement and the rf power). The total area
25 of both electrodes 20, 21 on which substrates 26, 25 can be placed (two substrates can be deposited in one process) is around 300 cm^2 . This gives rise to the value of silane utilisation factor (UF) in the range 30-60 %, which is an order of magnitude improvement over conventional PECVD techniques.

30 Figures 4 and 5 show the dependence of the a-Si:H deposition rate and the utilisation factor versus the silane flow rate. The difference between Figures 4 & 5 in the discharge confinement: the discharge confining gap d is 5 mm for Figure 4 and 2.5 mm for Figure 5. It is seen that an increase in the discharge confinement (a decrease in d) leads to an
35 increase in both the deposition rate and utilisation factor for similar silane flow rates. For a fixed discharge confinement the deposition rate increases

with the silane flow. This, however, occurs at the expense of the utilisation factor, which decreases with the silane flow rate. From a practical point of view this implies a trade-off between productivity (deposition rate) and running costs (silane consumption) when the optimum can be determined by the condition of minimum total cost of the product. As already mentioned both the deposition rate and the utilisation factor can be increased by increasing the discharge confinement (decreasing d) as shown in Figure 6. The increase in the rf power coupled into the discharge has a similar effect (Figure 7.).

As mentioned earlier, the previous work of C M Horwitz [C M Horwitz, J. Vac. Technol. 7,443 (1989)] on high rate deposition of amorphous silicon by the hollow cathode technique was done in the regime where deposition was accompanied by the gas phase polymerisation and powder formation, resulting in amorphous silicon films with defect (cluster) density unsuitable for any of the practical applications. In the present invention this problem is overcome by defining and operating in the region of the parameter space of the hollow cathode PECVD, where the gas phase polymerisation is avoided and defect free films are obtained.

For a certain level of rf power coupled into the discharge, there is a minimum pressure below which the gas phase polymerisation begins to occur in the central area of the hollow cathode region and, as the pressure is lowered further, it spreads towards the electrode periphery. This minimum pressure is inversely proportional to the rf power coupled into the discharge, so that the power to pressure ratio W/P should be maintained below a certain empirically established value in order to stay in the powder free regime. The limit for W/P decreases with the discharge confinement, i.e. for a constant pressure, in order to avoid an onset of the gas phase polymerisation, the discharge power should be reduced accordingly if the discharge confinement is increased, or, for a constant power level, a discharge confinement increase should be accompanied by an increase in the gas pressure. In addition, if the gas pressure, the discharge power and confinement are kept constant, silane dilution with noble gases (Ar, He) or hydrogen allows for an increase in the limit for W/P . Similar effect can be achieved by increasing the total (silane + dilution gas) gas flow rate.

The above definition of the polymerisation free parameter space of the hollow cathode PECVD is based on the following mechanism. Gas phase polymerisation proceeds through interaction between SiH_x species, when larger polymeric clusters can grow infinitely, since their precursors acquire negative (floating) potential and become suspended in plasma glow due to confinement by negative potential of the electrodes and the rf powered discharge confinement elements. This process occurs to some extent in the whole deposition parameter space, but begins to have a detrimental effect on the film quality when the concentration the polymerisation precursors in plasma volume exceeds a certain threshold, where avalanche gas phase polymerisation occurs. This results in deposition of films with defect density unacceptable for practical applications. The principle of the high density hollow cathode discharge is based on confinement of the energetic secondary electrons released from the rf powered electrodes. As the degree of this confinement increases the plasma density increases as well. At the same time, however, this causes an increase in the confinement of the negatively charged clusters/polymerisation precursors so that their concentration may exceed the avalanche polymerisation threshold. This sets a limit for the discharge confinement in order to avoid the gas phase polymerisation. As the discharge power increases the confining potentials also increase having an effect similar to the increase in the confinement itself. Dilution of silane helps to reduce the effective concentration of polymerisation precursors, while an increase in the total gas flow promotes their removal from the hollow cathode zone towards the pump port. The increase in the process pressure reduces the effective discharge confinement via the hollow cathode glow region extending further beyond the physical confinement space as defined by the discharge confinement elements. All this helps to remove the cluster precursors from the hollow cathode zone and therefore to reduce their concentration below the gas phase polymerisation threshold.

In practice, an empirically established limit for the power to pressure ratio can be used in order to prevent the degradation of film quality due to an onset of gas phase polymerisation. As follows from the above discussion, this limit is lower for increased discharge confinement and higher for increased total gas flow and/or silane dilution. This is

illustrated in Figure 11, which shows power to pressure ratios on the boundary of the gas phase polymerisation zone for three different sets of discharge confinement, total gas flow and silane dilution.

The ion-bombardment during a-Si:H deposition in a HCPECVD system is usually greater than in the conventional diode PECVD system. The ion-bombardment is usually beneficial since it can increase the density of a-Si:H material, however, for some applications a reduced ion bombardment may be required. Referring to Figure 10, a controlled reduction ion-bombardment can also be achieved by spacing each substrate from its respective electrode by a distance of 2 - 3 mm while it still remains within the dark space. The spacing can be maintained by locating a spacing element 36 between the substrate and electrode as illustrated. This arrangement reduces the ion acceleration energy and thus reduces ion-bombardment.

Commercial versions of the Hollow Cathode reactor

The Hollow Cathode system can be scaled to accommodate large area substrate as required for solar module and liquid crystal display (LCD) applications. Figure 8 shows a schematic of HCPECVD "box coater" in which a series of HCPECVD boxes 34 are connected, with the unit box frame commonly grounded. Figure 9 shows the detail of a single HCPECVD box 34 including the chamber 40, plasma confinement elements 45, gas delivery tubes 46, electrodes 41, 42 and glass substrates 43, 44. The chamber frame 40 is grounded with two rf electrodes 41, 42 separately placed on either side of the reactor. Two pieces of glass 43, 44 are placed facing each other and with each adjacent to an rf electrode. Two gas delivery tubes 46 are positioned between the gap 47 in the plasma confinement element 45.

Alternatively, without the use of gas delivery tubes 46, the gas can be introduced in the gap behind each of the electrodes 41,42 through a set of holes in the grounded wall 40 of the HCPECVD box and will then enter the hollow cathode discharge zone through the gaps between confining elements 45. The HCPECVD box coater has the advantages of achieving higher values of the utilisation factor and the deposition rate.

Features

The preferred embodiment of the HCPECVD has the following features which give advantages over conventional PECVD for a-Si:H deposition.

5 Hydrogenated amorphous silicon films can be deposited simultaneously on two metal or dielectric substrates 25, 26, 43, 44 from a radio frequency glow discharge 32 maintained in a mixture of gases or vapours with at least one of them containing silicon in its molecule. The discharge 32 is maintained between two mutually symmetric, radio
10 frequency powered electrodes 20, 21, 41, 42 enclosed in a grounded chamber 22, 40 and isolated from it, with one substrate placed on the internal side of each of the electrodes 20, 21, 41, 42.

All surfaces of the electrodes 20, 21, 41, 42 except the two surfaces where the substrates 25, 26, 43, 44 are placed, are enclosed in grounded
15 metal parts 28, some of which may be chamber walls, with a gap between them sufficiently small to prevent discharge formation at the process pressures.

The method can be extended so that $2n$ ($n=1,2,3..$) substrates are deposited simultaneously in each of n pairs of the electrodes such as by
20 using a "box-coater" arrangement particularly well suited to the hollow cathode configuration.

The substrate temperature during the deposition can be controlled by grounded heaters located behind the electrodes and conforming in shape to the back surface of the heaters.

25 In case of the multiple plasma box configuration, the heating of the chamber can be realised by flowing a hot gas through the chamber.

Discharge characteristics and related deposition process and film characteristics can be controlled by confining the discharge by metal parts connected either to the electrodes or to the chamber in a way that
30 preserves the symmetry of the system with respect to each of the substrates.

The confining parts connected to the electrodes can be shielded from the grounded chamber by grounded parts that are shaped to conform with the electrode back surfaces.

35 The ion bombardment energy on the substrate surface and related film characteristics can be controlled by introducing and varying equal

gaps between the back surfaces of each of the substrates and the electrodes. These gaps can be filled with dielectric material.

The two electrodes can be fixed on a grounded metal frame, but isolated from it, thus forming a portable process vessel which can be loaded in the chamber for the deposition and then unloaded from it.

Silicon tetrahydride (silane) is believed to be the most suitable silicon containing gas.

The silane can be diluted with either noble gases or hydrogen or with both.

The product of W^k/P , where W is the power density on the substrate (W/cm^2), P is the gas pressure and k is a coefficient ranging from 0.5 to 4.00, is kept below an empirically established value, in order to prevent the degradation of film quality due to an on-set of gas phase polymerisation the value being lower for increased discharge confinement and higher for increased total gas flow and/or increased silane dilution. This value ranges from 0.25 to 2.04 as determined from the experimental HCCVD reactor for which 3 examples for different operating conditions are given in Figure 11.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

CLAIMS:

1. A method of deposition of hydrogenated amorphous silicon film onto a substrate from a radio frequency glow discharge, the method including, placing the substrate on or near an internally facing surface of a first electrode of a pair of mutually symmetric, radio frequency powered,
5 electrodes enclosed in and isolated from, a grounded chamber, evacuating the chamber, and introducing into the chamber, a gas or vapour or a mixture of gasses and/or vapours including a source of silicon atoms and operating the chamber with a power to pressure ratio determined to allow
10 rapid formation of amorphous silicon on the substrate with dominant monohydride (Si:H) bonds and low particle formation at a rate greater than 15 Å/sec.
2. The method of claim 1 wherein, the chamber is grounded and the opposed electrodes are maintained at the radio frequency potential of the
15 power supply.
3. The method of claim 2 wherein, in use, a substrate is located on a respective internally facing surface of each of the opposed electrodes such that two substrates are coated simultaneously.
4. The method of claim 3 wherein, all surfaces of the opposed
20 electrodes, except those covered by a substrate are enclosed in grounded metal shields separated from the respective surfaces by a gap of a size selected to prevent discharge formation at the process pressure.
5. The method of claim 3 or claim 4 wherein, a plurality (n) of pairs of opposed electrode surfaces are provided in the chamber with each pair
25 of opposed surfaces arranged to receive a respective pair of substrates for deposition.
6. The method of claim 5 wherein, each pair of opposed electrode surfaces is provided by a separate pair of electrodes located in a grounded enclosure within the chamber and electrode pairs are removable
30 individually as a module for substrate attachment and removal.
7. The method of claim 6 wherein, two electrodes are fixed to and insulated from, a grounded metal frame to form a portable process vessel which is arranged to be loaded into the chamber for deposition and then unloaded from it.

8. The method of claim 5 wherein, the electrode surfaces are provided by two single sided end electrodes and one or more two sided intermediate electrodes, the single side of each end electrode and both sides of each intermediate electrode being arranged to accept a substrate for deposition with each surface of each electrode providing one of a different pair of opposed surfaces to the other surface of the same electrode, and each electrode is removable for attachment and removal of substrates.

9. The method as claimed in any one of claims 1 to 8, wherein substrate temperature is controlled by grounded heaters associated with each electrode.

10. The method of claim 9 wherein heaters are located behind each electrode, shaped to conform with the shape of the back surface of the electrode,

11. The method of claim 9 wherein, the electrodes may have internal spaces in which the heaters are located.

12. The method as claimed in any one of claims 1 to 8 wherein the process temperature is controlled by controlling the temperature of gasses introduced into the chamber.

13. The method as claimed in any one of claims 1 to 12 wherein discharge confining elements, are located within the chamber and connected to the electrodes and/or the chamber to control the discharge characteristics, deposition process and film characteristics.

14. The method of claim 13 wherein, the discharge confining elements are of metal construction.

15. The method of claim 13 or 14, wherein the confining elements are configured to preserve the symmetry of the system with respect to the substrates.

16. The method of claim 13, 14 or 15, therein the confining elements are connected to the electrode and are shielded from the grounded chamber by shielding elements conforming with back surfaces of the confining elements and separated from the confining elements by a gap sufficiently small to prevent discharge formation in the gap.

17. The method as claimed in any one of claims 1 to 16, wherein film characteristics are controlled by controlling the ion bombardment energy on the surface of the substrate.

18. The method of claim 17 wherein the control of the bombardment energy on the surface of the substrate is achieved by introducing an equal gap between each of the substrates on each pair of opposed electrode surfaces and the respective electrode surface, and adjusting the gap to
5 achieve the desired characteristics.

19. The method of claim 17 wherein each of the gaps between the substrates and the respective electrodes are filled with dielectric material.

20. The method as claimed in any one of claims 1 to 19, wherein silicon tetrahydride (silane) is used as the silicon source and the source
10 gas may be diluted with a noble gas or hydrogen or both.

21. The method as claimed in any one of claims 1 to 20, wherein the ratio W^k/P , where W is power density on the substrate (W/cm^2), P is the gas pressure (pa) and k is a co-efficient ranging from 0.5 to 4.0, is kept below a predetermined, empirically established, value in order to prevent the
15 degradation of film quality due to an onset of gas phase polymerisation.

22. The method as claimed in any one of claims 1 to 20, wherein the ratio W^k/P , where W is power density on the substrate (W/cm^2), P is the gas pressure (pa) and k is a co-efficient ranging from 1.47 to 1.56, is kept below a predetermined, empirically established, value in order to prevent
20 the degradation of film quality due to an onset of gas phase polymerisation.

23. The method of claim 21 or 22, wherein the value for W^k/P is lower, for increased discharge confinement and higher for increased total gas flow rate and/or increased silane dilution with a noble gas or hydrogen or
25 both

24. The method of claim 21, 22 or 23, wherein the value for W^k/P is in the range from 0.25 to 2.04.

25. A Plasma Enhanced Chemical Vapour Deposition (PECVD) system for depositing hydrogenated amorphous silicon films including a chamber enclosing a pair of mutually symmetric, opposed electrodes, at least one of
30 the opposed electrodes being arranged to receive a deposition substrate on or adjacent to its surface, the chamber including an output port connected to a vacuum pump and an input port connected to a supply of a gas or vapour or gases and/or vapours including a source of silicon atoms, and a
35 radio frequency power supply connected between the chamber and the pair of symmetric electrodes and control means for setting a pressure to

power ratio at a value determined to cause formation of amorphous silicon on the substrate at a rate greater than 15 Å/sec with dominant monohydride (Si:H) bonds and low particle formation.

26. The system of claim 25 wherein the chamber is grounded and the radio frequency/ power supply is connected between the grounded chamber and each of the electrodes.

27. The system of claim 26 wherein in use, a substrate is located on a respective internally facing surface such that two substrates are coated simultaneously.

28. The system of claim 27 wherein all surfaces of the opposed electrodes, except those covered by a substrate are enclosed in grounded metal shields separated from the respective surfaces by a gap of a size selected to prevent discharge formation at the process pressure.

29. The system of claim 27 or claim 28 wherein a plurality (n) of pairs of opposed electrode surfaces are provided in the chamber with each pair of opposed surfaces arranged to receive a respective pair of substrates for deposition.

30. The system of claim 29 wherein each pair of opposed electrode surfaces is provided by a separate pair of electrodes located in a grounded enclosure within the chamber and electrode pairs are removable individually as a module for substrate attachment and removal.

31. The system of claim 30 wherein two electrodes are fixed to and insulated from, a grounded metal frame to form a portable process vessel which is arranged to be loaded into the chamber for deposition and then unloaded from it.

32. The system of claim 31 wherein the electrode surfaces are provided by two single sided end electrodes and one or more two sided intermediate electrodes, the single side of each end electrode and both sides of each intermediate electrode being arranged to accept a substrate for deposition with each surface of each electrode providing one of a different pair of opposed surfaces to the other surface of the same electrode, and each electrode is removable for attachment and removal of substrates.

33. The system as claimed in any one of claims 25 to 32, wherein grounded heaters associated with each electrode are provided to control substrate temperature.

34. The system of claim 31, wherein heaters are located behind each electrode, shaped to conform with the shape of the back surface of the electrode,

35. The system of claim 32, wherein the electrodes are provided with
5 internal spaces in which the heaters are located.

36. The system as claimed in any one of claims 25 to 35, wherein temperature control means are provided to control the temperature of gasses introduced into the chamber.

37. The system as claimed in any one of claims 25 to 36, wherein
10 discharge confining elements, are located within the chamber and connected to the electrodes and/or the chamber to control the discharge characteristics, deposition process and film characteristics.

38. The system of claim 37 wherein the discharge confining elements are of metal construction.

39. The system of claim 37 or 38, wherein the confining elements are
15 preferably configured to preserve the symmetry of the system with respect to the substrates.

40. The system of claim 37, 38 or 39, wherein the confining elements are connected to the electrode and are shielded from the grounded
20 chamber by shielding elements conforming with back surfaces of the confining elements and separated from the confining elements by a gap of a size selected to prevent discharge formation in the gap.

41. The system as claimed in any one of claims 25 to 40, controlling means are provided to control the ion bombardment energy, the ion
25 bombardment energy on the surface of the substrate.

42. The system of claim 41, wherein the ion bombardment energy control means includes a substrate support means arranged to introduce an equal gap between each of the substrates on each pair of opposed electrode surfaces and the respective electrode surface, the resultant gap
30 being adjustable to achieve the desired characteristics.

43. The system of claim 42, wherein the gaps between the substrates and the respective electrodes are filled with dielectric material.

44. The system as claimed in any one of claims 25 to 43, wherein silicon tetrahydride (silane) is used as the silicon source and the source
35 gas may be diluted with a noble gas or hydrogen or both.

45. The system as claimed in any one of claims 25 to 44, wherein the ratio W^k/P , where W is power density on the substrate (W/cm^2), P is the gas pressure (pa) and k is a co-efficient ranging from 0.5 to 4.0, is kept below a predetermined, empirically established, value in order to prevent the degradation of film quality due to an onset of gas phase polymerisation.

46. The system of claim 45, wherein the co-efficient k is in the range 1.47 to 1.56.

47. The system of claim 45 or 46, wherein the value for W^k/P is lower, for increased discharge confinement and higher for increased total gas flow rate and/or increased silane dilution with a noble gas or hydrogen or both.

48. The system of claim 45, 46 or 47, wherein the value for W^k/P is in the range from 0.25 to 2.04.

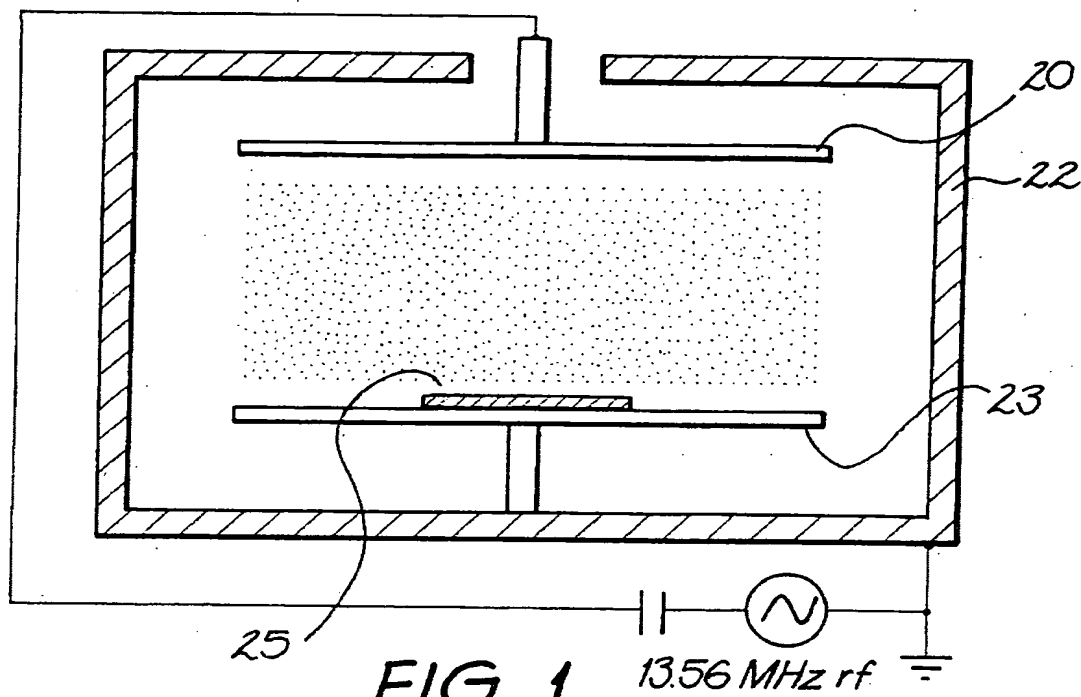


FIG. 1
PRIOR ART

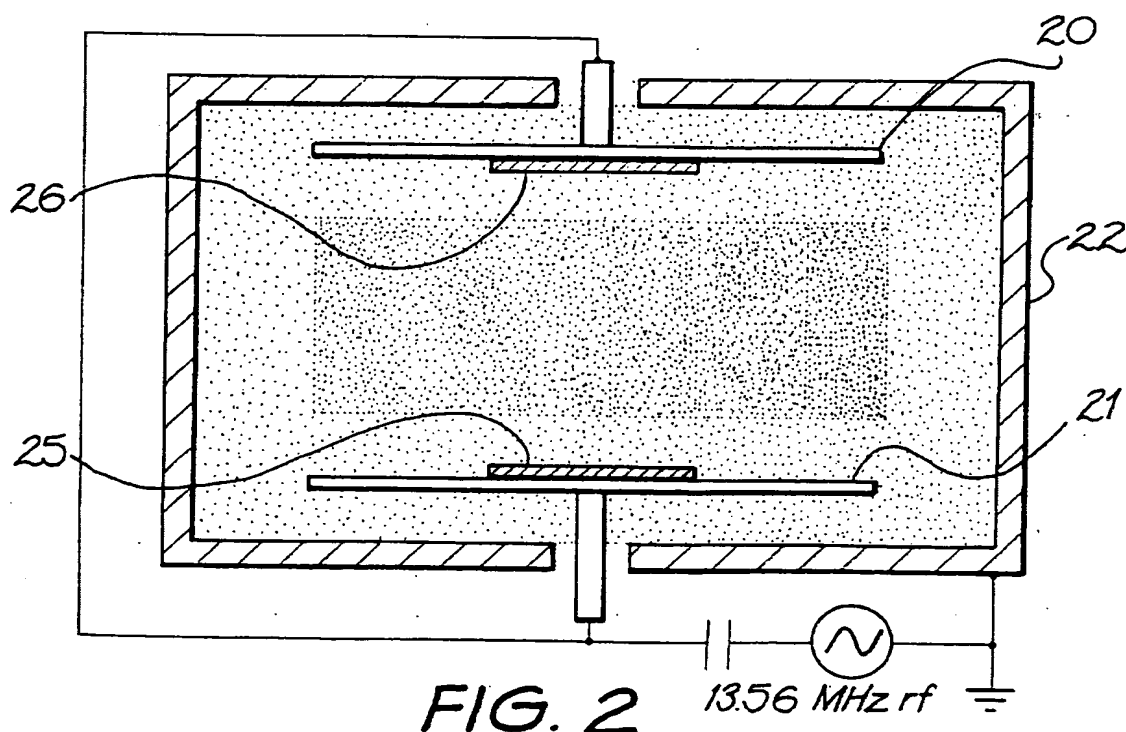


FIG. 2

SUBSTITUTE SHEET (Rule 26) (RO/AU)

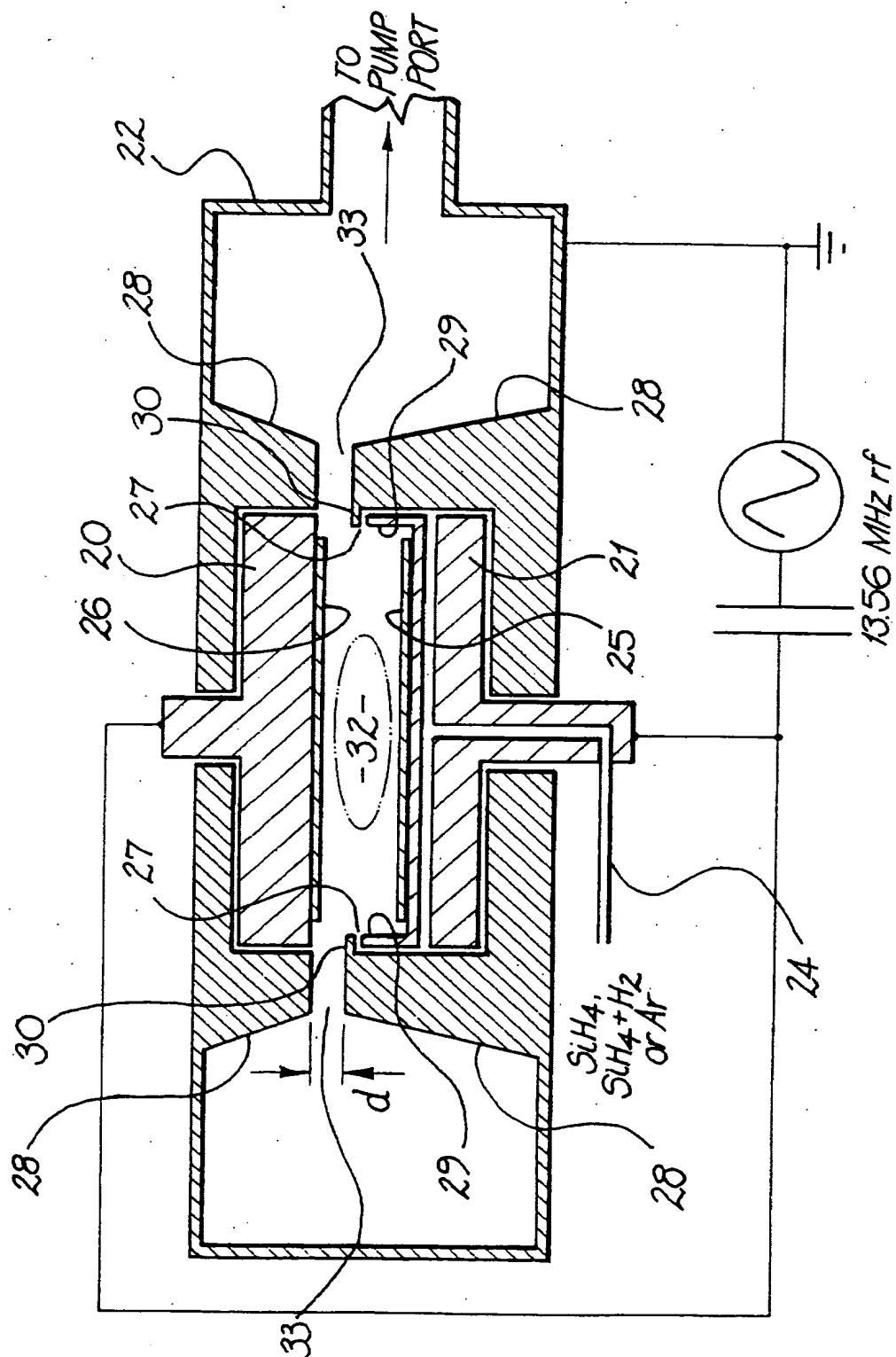


FIG. 3

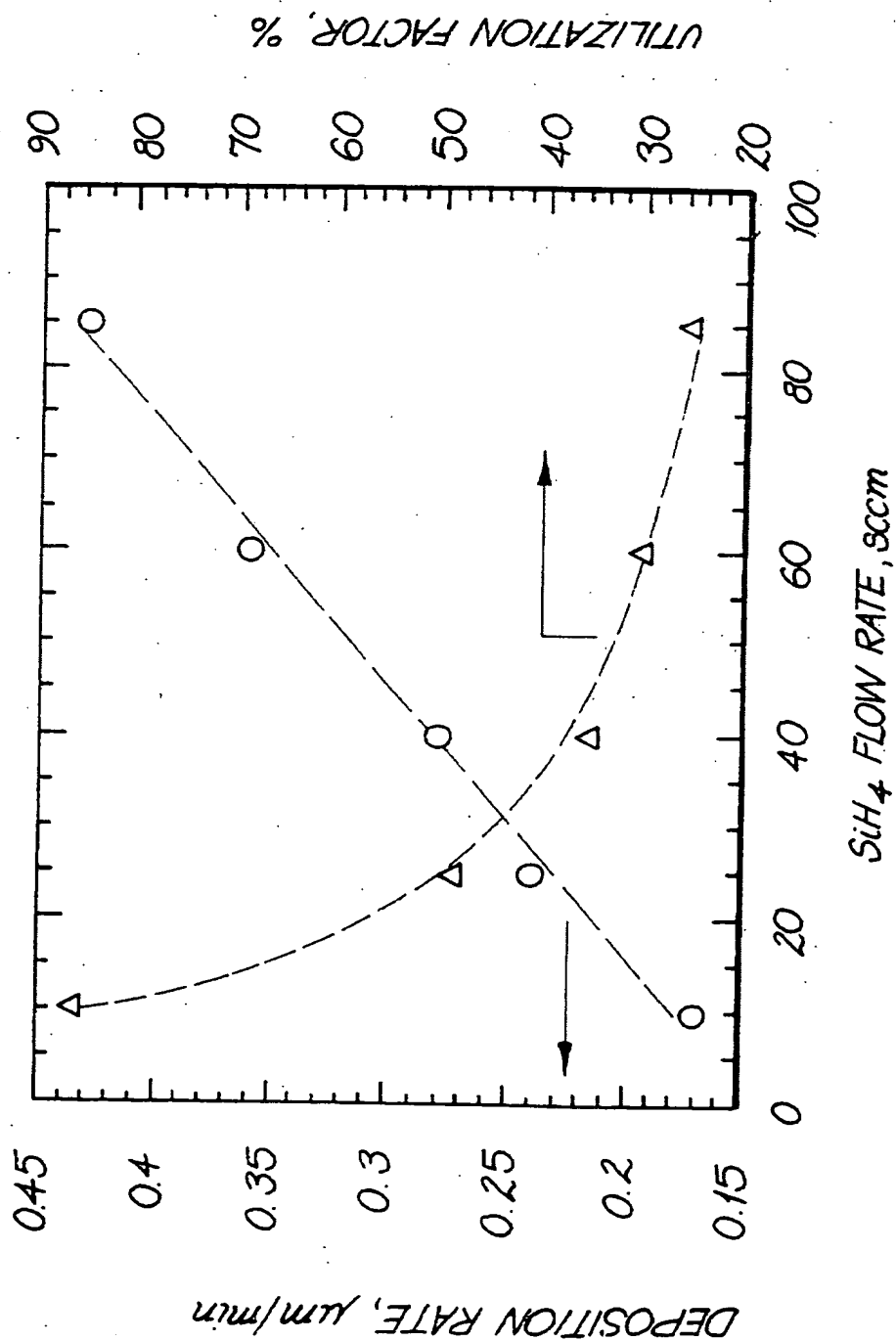


FIG. 4

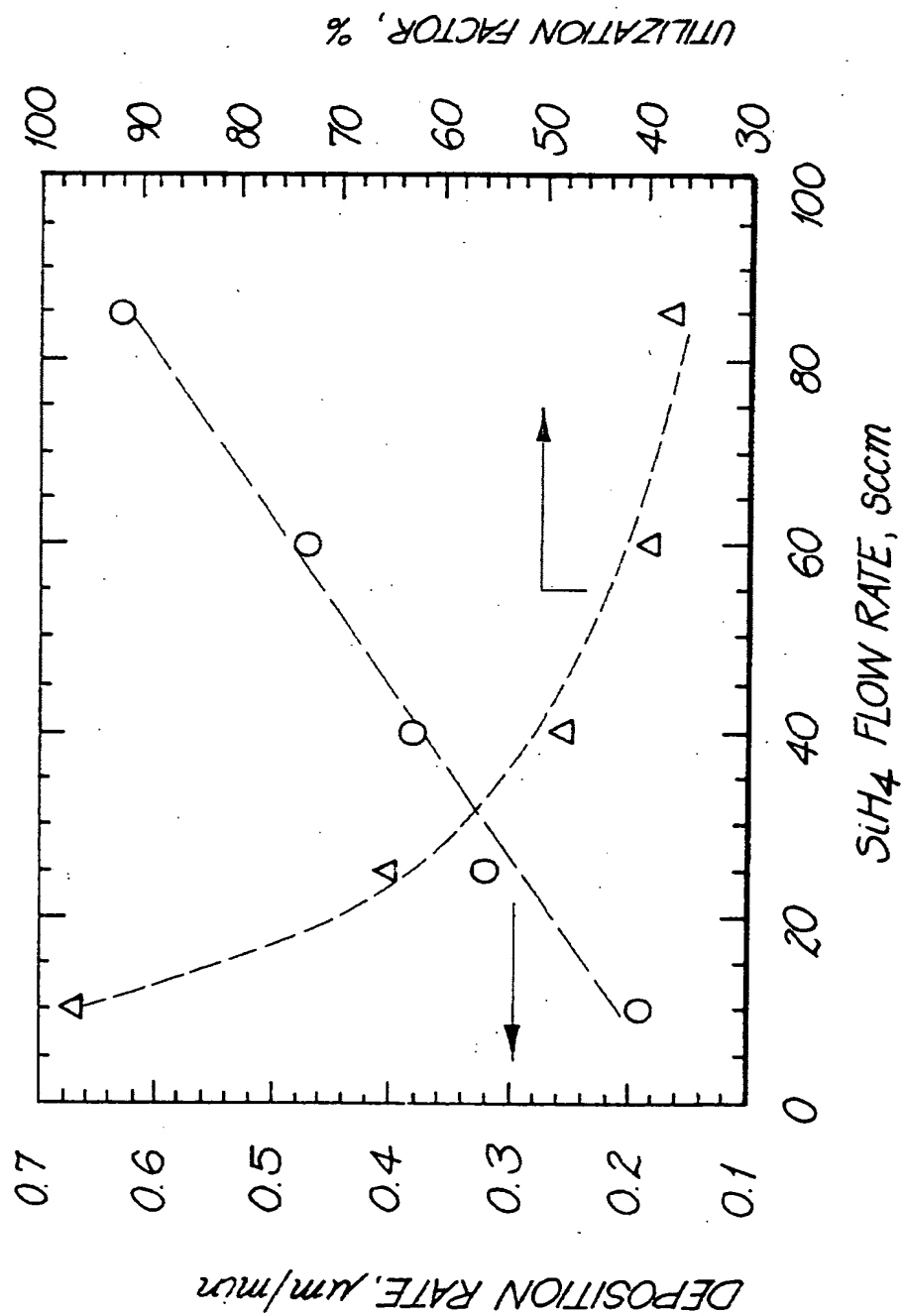


FIG. 5

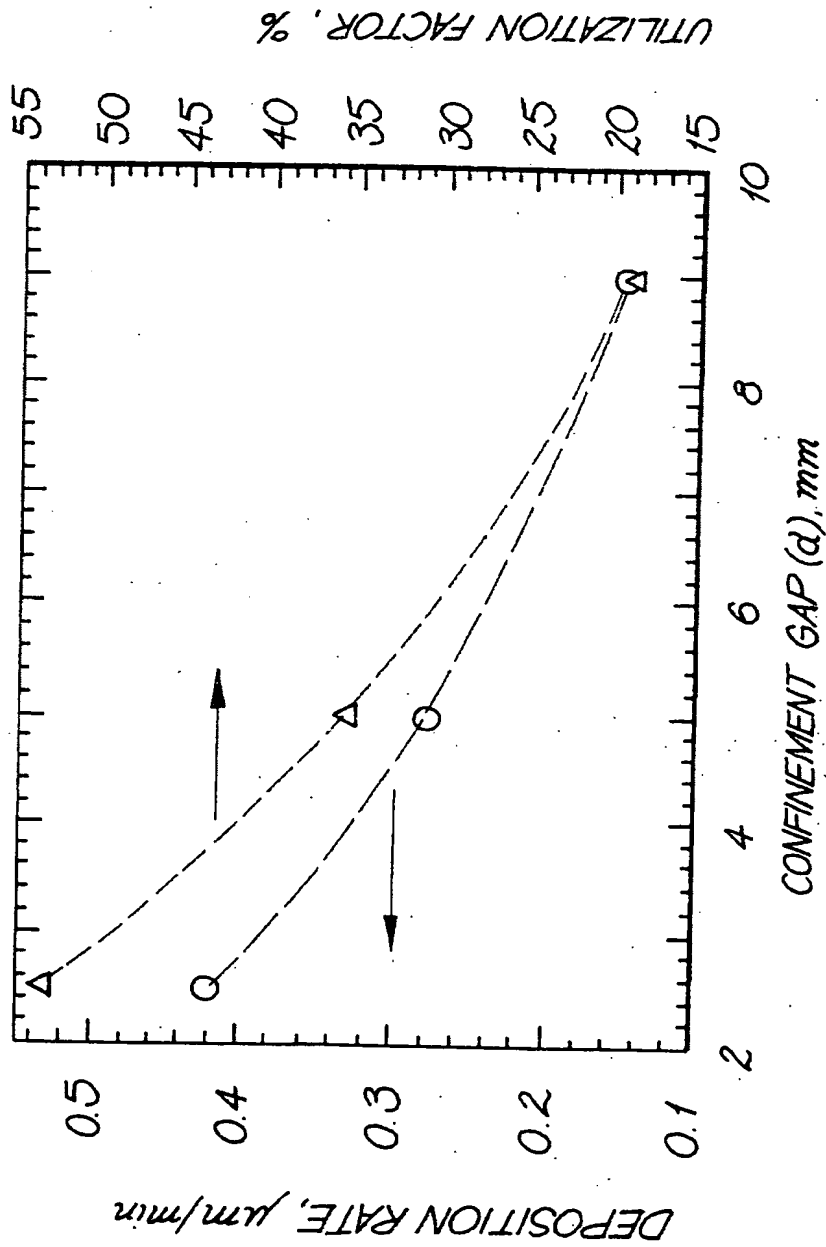


FIG. 6

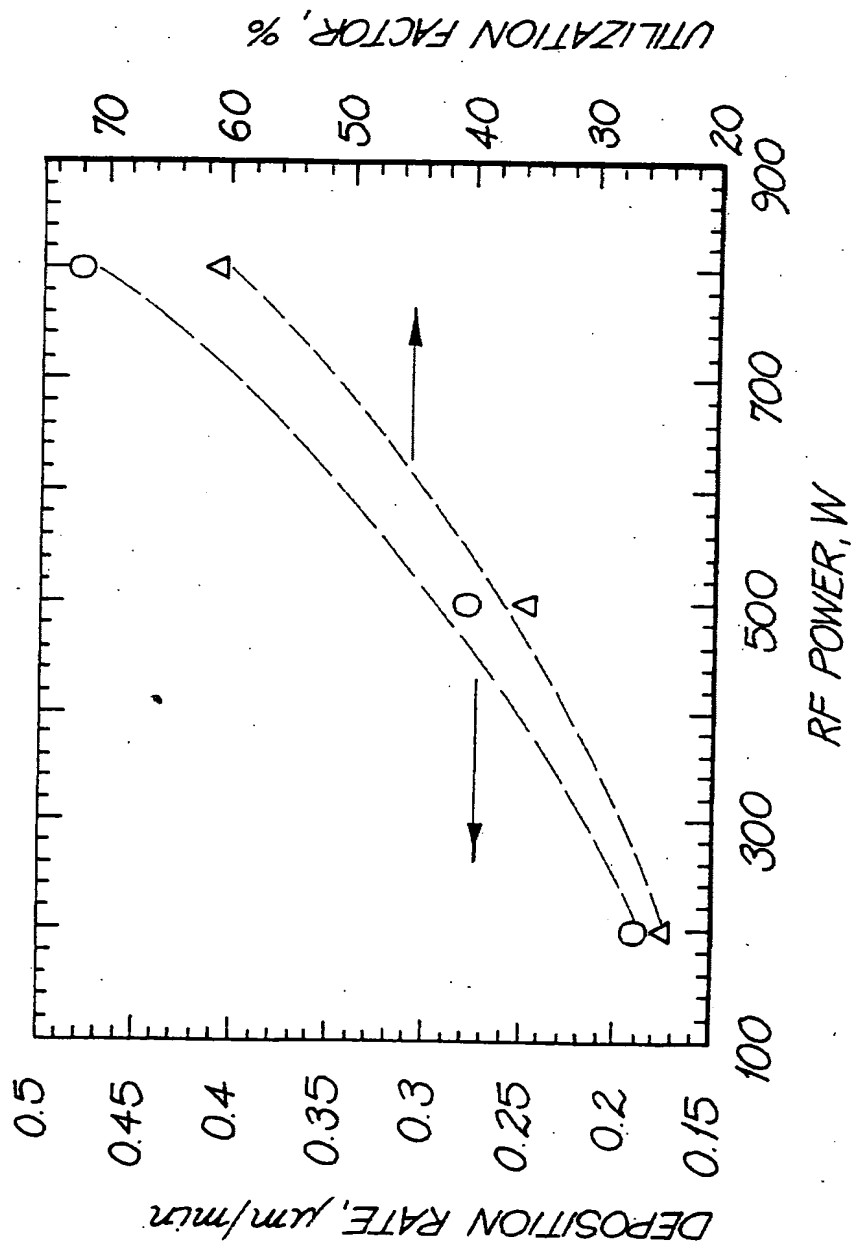


FIG. 7

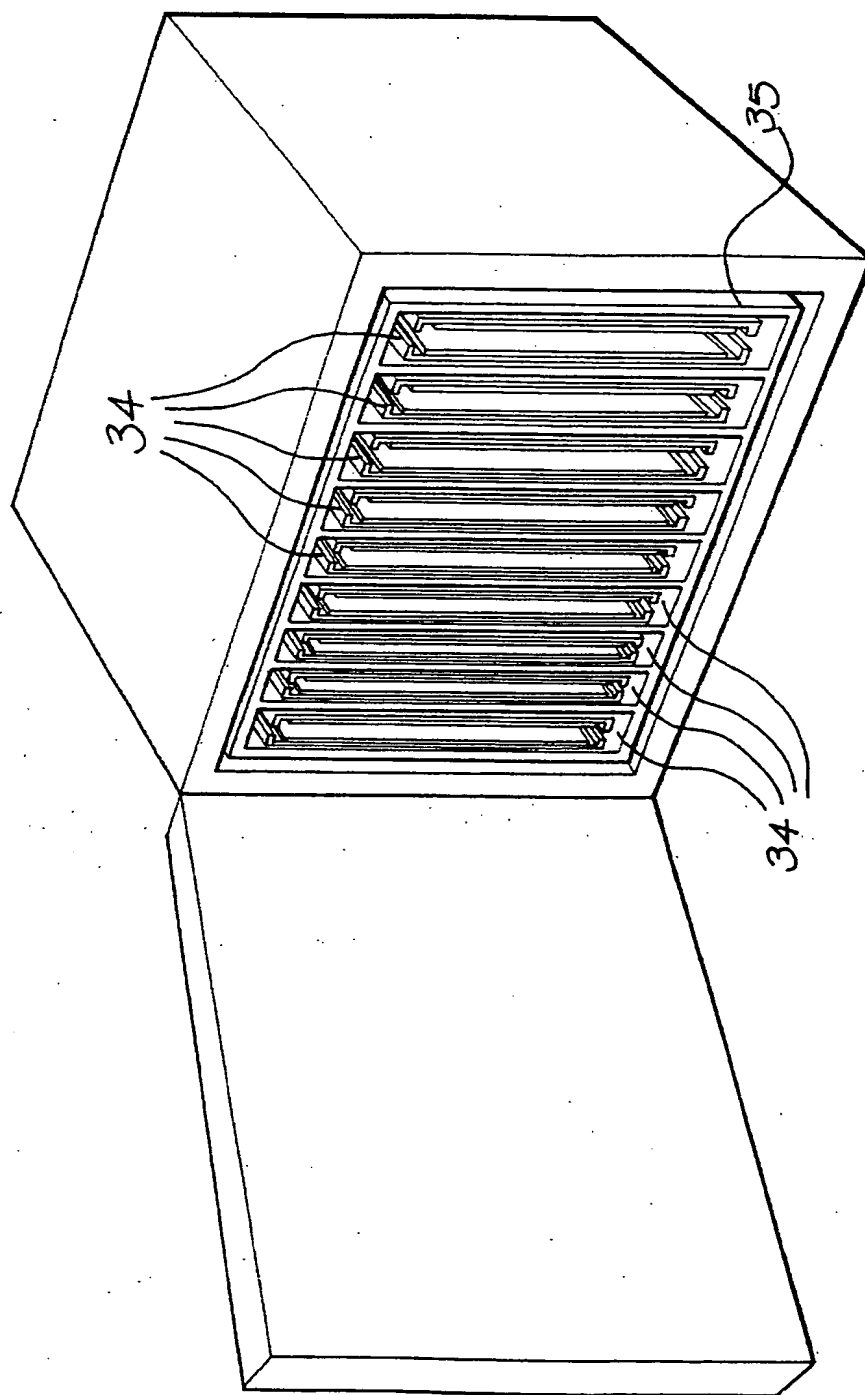


FIG. 8

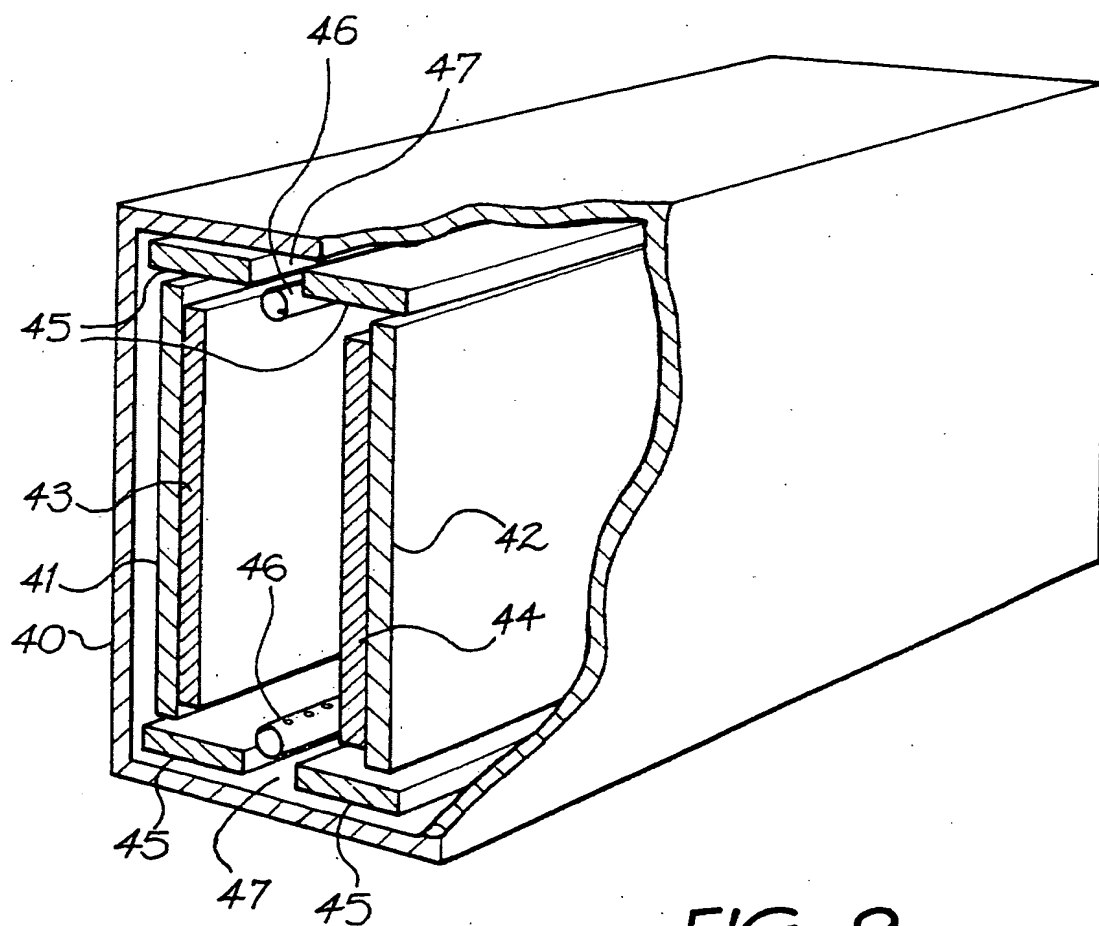


FIG. 9

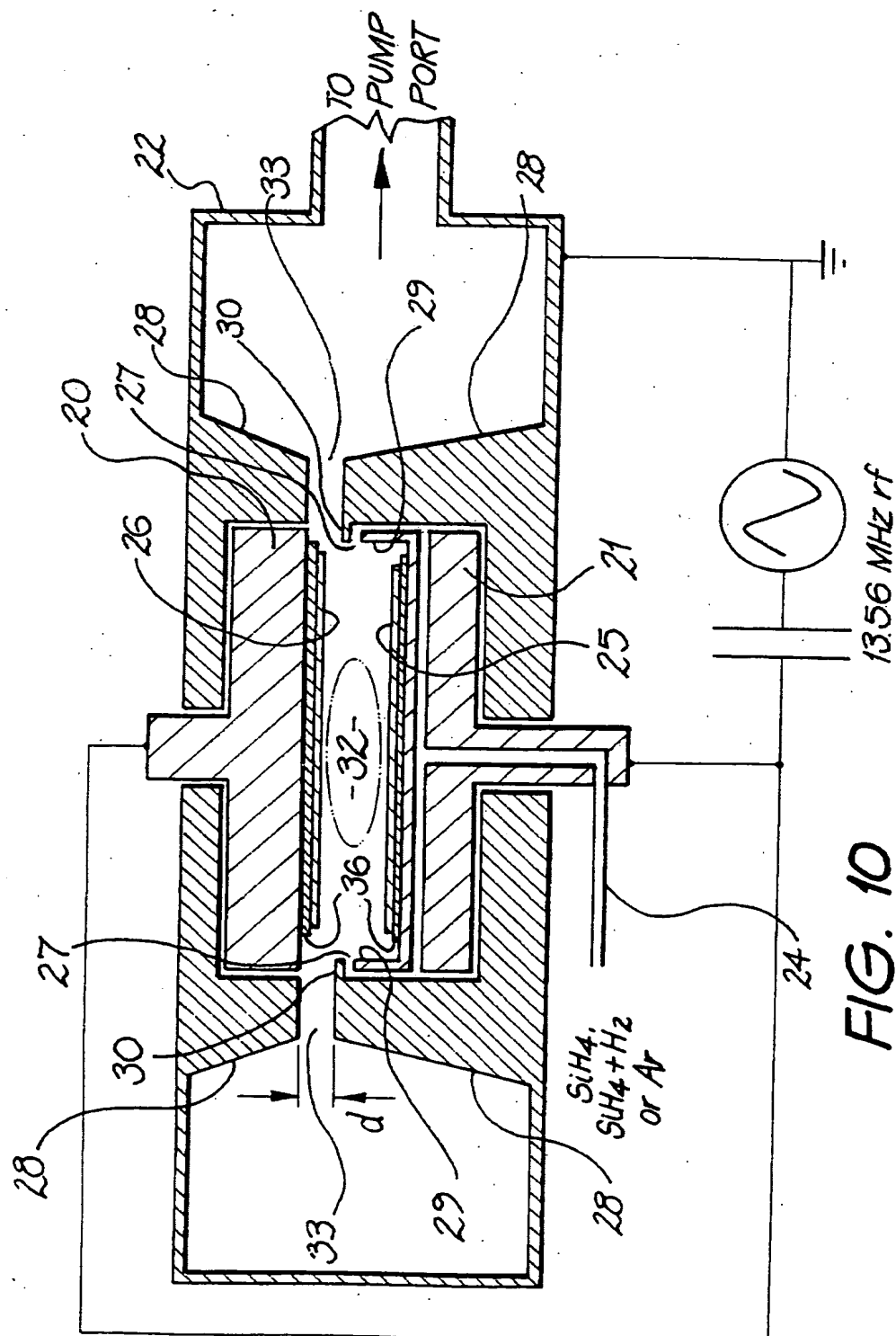


FIG. 10

EXAMPLE 1. POWDER FORMATION FOR $W^{1.65}/P > 1.05$

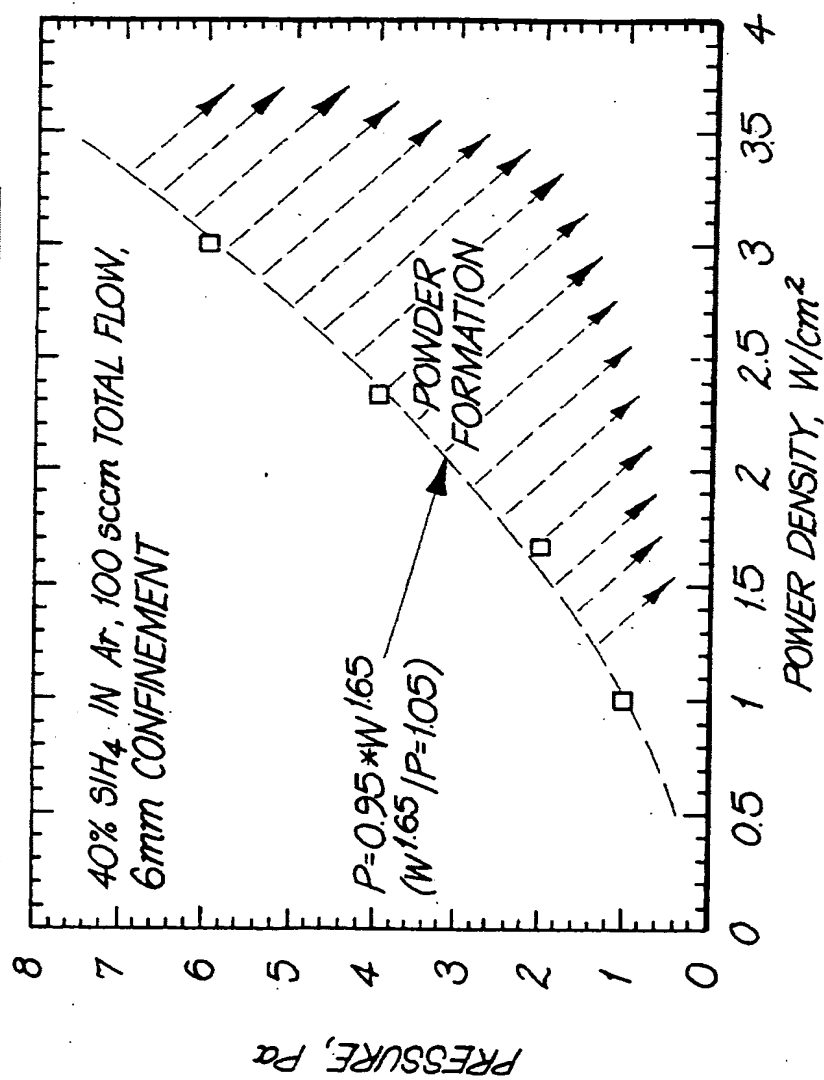


FIG. 11a

EXAMPLE 2. POWDER FORMATION FOR $W^{1.61}/P > 0.25$

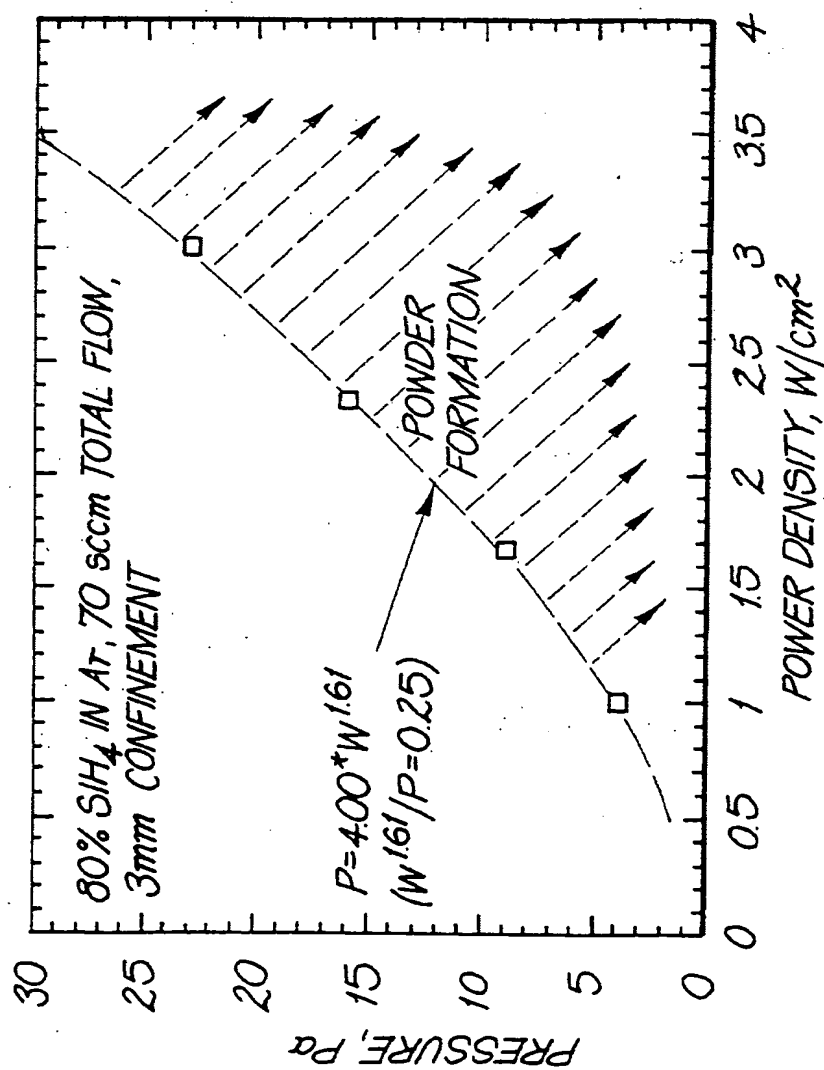


FIG. 11b

EXAMPLE 3, POWDER FORMATION FOR $W^{1.47}/P > 2.04$

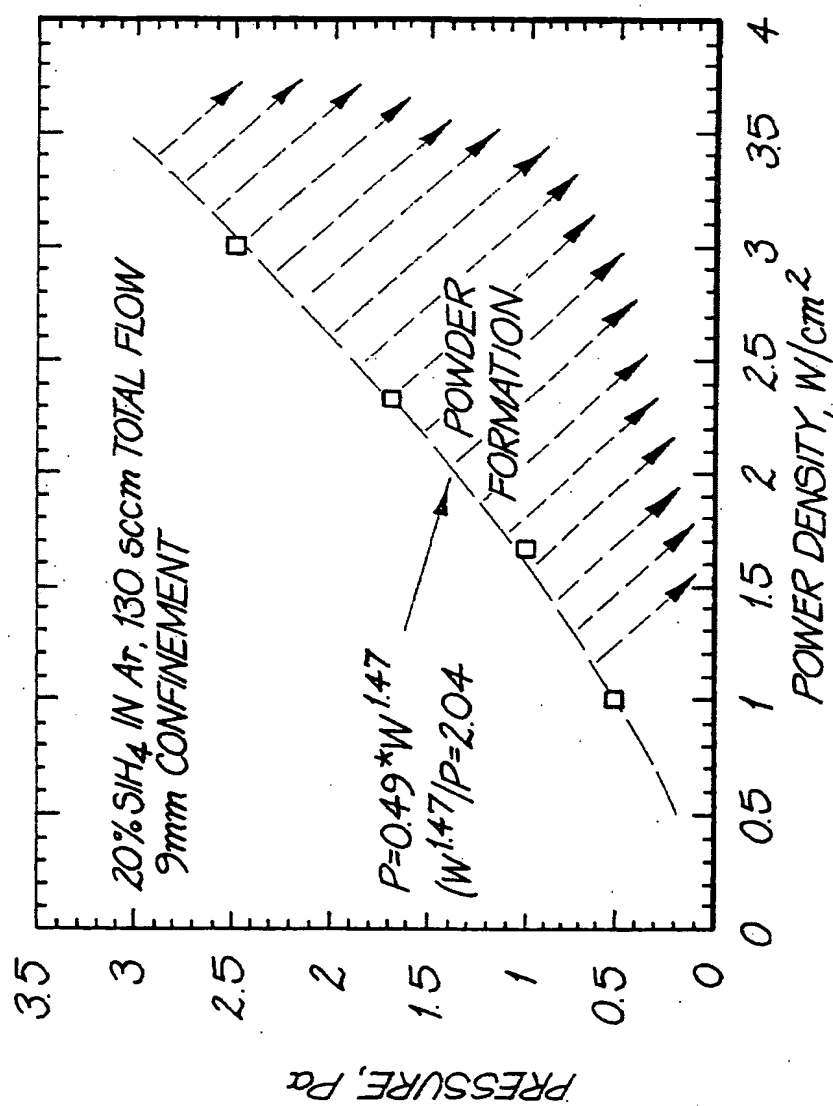


FIG. 11C

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU 98/00974

A. CLASSIFICATION OF SUBJECT MATTER												
Int Cl ⁶ : C23C 16/24, 16/52; H01L 21/203												
According to International Patent Classification (IPC) or to both national classification and IPC												
B. FIELDS SEARCHED												
Minimum documentation searched (classification system followed by classification symbols) C23C 16/24, 16/52; H01L 21/203												
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU: IPC as above												
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Derwent WPAT, JAPIO												
C. DOCUMENTS CONSIDERED TO BE RELEVANT												
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.										
A	US 5585149 A (HIRAI) 17 December 1996	1, 25										
A	US 5487786 A (CHIDA) 30 January 1996	1, 25										
A	US 5133986 A (BLUM) 28 July 1992	1, 25										
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex												
<p>* Special categories of cited documents:</p> <table border="0"> <tr> <td>"A" document defining the general state of the art which is not considered to be of particular relevance</td> <td>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>"E" earlier application or patent but published on or after the international filing date</td> <td>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>"O" document referring to an oral disclosure, use, exhibition or other means</td> <td>"&" document member of the same patent family</td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family	"P" document published prior to the international filing date but later than the priority date claimed	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention											
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone											
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art											
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family											
"P" document published prior to the international filing date but later than the priority date claimed												
Date of the actual completion of the international search 1 February 1999		Date of mailing of the international search report 16 FEB 1999										
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No.: (02) 6285 3929		Authorized officer JAMES DZIEDZIC Telephone No.: (02) 6283 2495										

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 98/00974

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5061511 A (SAITOH) 29 October 1991	1, 25
A	US 4933203 A (CURTINS) 12 June 1990	1, 25
A	US 4792460 A (CHU) 20 December 1988	1, 25
A	US 4631198 A (KAKINUMA) 23 December 1986	1, 25
A	US 4448801 A (FUKUDA) 15 May 1984	1, 25
A	US 4405656 A (SHIMIZU) 20 September 1983	1, 25

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/AU 98/00974

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
UA	5585149	AU	42715/78	CA	1166505	DE	2855718
		FR	2412874	FR	2487535	GB	2013725
		GB	2102028	HK	424/88	JP	54086341
		US	4265991US	US	4451547	US	4507375
		US	4552824	US	5576060	US	5640663
		US	5658703	US	5756250		
US	5487786	EP	659905	JP	7230960		
US	5133986	EP	478984	JP	4234111		
US	5061511	DE	3742110	JP	6314382	US	4957772
UA	4933203	CH	668145	EP	263788	JP	63197329
US	4792460	JP	63021210				
US	4631198	JP	59232909				
US	4448801	DE	3124447	GB	2081745	JP	57010920
US	4405656	DE	3140994	GB	2087930	JP	57067938
END OF ANNEX							